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Ultraviolet studies of hydrogen-bonding in isomeric toluidines

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Hydrogen bond in toluidines in binary and ternary mixtures in different solvents has been studied by the methods of ultraviolet spectroscopy. The association equilibrium constants K and the hydrogen bonding energies ($-\Delta H$) have been measured. It is observed that values of $-\Delta H$ are in the order para-toluidine > meta-toluidine > ortho-toluidine. Part played by steric hindrance in the case of the ortho isomer has been pointed out. Effect of intermolecular hydrogen bond on the frequency and intensity of absorption bands due to electronic transitions in the toluidines is also discussed. It has been concluded that on N--H .... O bond formation, binding energy of the sp^2 hybridized lone pair on nitrogen in toluidine molecules decreases so that their interaction with π-system increases leading to a large migration moment.

1 Introduction

Hydrogen bond is generally studied by methods of infrared spectroscopy. However, ultraviolet spectroscopy is also known to furnish information of intermolecular association (Nagakura *et al*, 1952) and an estimate of the energy of hydrogen bond formation (Nagakura, 1954) can be made. Most of the earlier works in this field were concerned with frequency changes (Pimentel 1957) while only a few authors (Baba *et al* 1961) dealt with change in intensity. Intermolecular hydrogen bonding between toluidines and proton acceptor solvents was shown to exist in earlier infrared studies (Medhi *et al* 1962). In a programme of work undertaken recently, the electronic spectra of ortho-, meta- and para-toluidines were investigated in *neutral* and *proton-acceptor* solvents with the object of analysing the changes in frequency and specially, the intensity of the bands.

2. Experimental

Spectroscopically pure cyclohexane was supplied by B.D.H. Chemically pure dioxane was purified by distillation under reduced pressure. Ortho- and meta-toluidine were subjected to fractional distillation and the collected fractions were subjected to distillation under reduced pressure. This operation was repeated four times before the samples were used. Paratoluidine was recrystallized from ethyl alcohol. This operation was repeated five to six times till white coloured crystals of paratoluidine were obtained. Melting point of the compound was then determined. The sample was kept in a vacuum desiccator.

Ultraviolet absorption spectra were measured with a Hilger UV spectrophotometer at different temperatures and 1 cm absorption cells were used. For every wavelength, the slit width was maintained at a definite value. For this purpose a wavelength-slit calibration chart was prepared beforehand. Silica-gel capsules (used in the spectrophotometer) were changed twice in a day to keep the instrument free from moisture.

Procedure

Taking the three component systems viz, isomeric toluidines, dioxane and cyclohexane, the last compound being the inert solvent, a set of absorption spectra was measured. In actual practice, dioxane concentration was increased in steps from 0 to 0.5 mole/litre. In every measurement the mixture of cyclohexane and dioxane, in which concentration of dioxane was identical with that in the sample solution (cyclohexane-dioxane-toluidine), was taken as reference. The measurements were made at the three different temperatures (293°K, 303°K and 313°K).

The association equilibrium constant (K) was calculated by the equation (Baba and Suzuki, 1961)

$$\frac{1}{\varepsilon-\varepsilon_f} = \frac{1}{K}\cdot\frac{1}{\varepsilon_b-\varepsilon_f}\cdot\frac{1}{C}+\frac{1}{\varepsilon_b-\varepsilon_f} \qquad \ldots\ldots\ldots (1)$$

where ε_f = molar extinction coefficient of the non-hydrogen bonded molecule, ε = molar extinction coefficient for a solution in which dioxane concentration is C and ε_b = moler extinction coefficient for the hydrogen-bonded molecule.

All these extinction coefficients refer to a given frequency. Graphs were plotted taking $1/(\varepsilon-\varepsilon_f)$ as ordinate and $1/C$ as abscissa. In every case, an almost linear graph was obtained (fig 1). On extrapolating the straight line to the point where $(1/\varepsilon-\varepsilon_f) = 0$, the equilibrium constant was obtained as, $K = -1/C$.

The free enery changes of the systems of isomeric toluidines were calculated from the familiar equation,

$$\Delta F = -RT \ln K \tag{2}$$

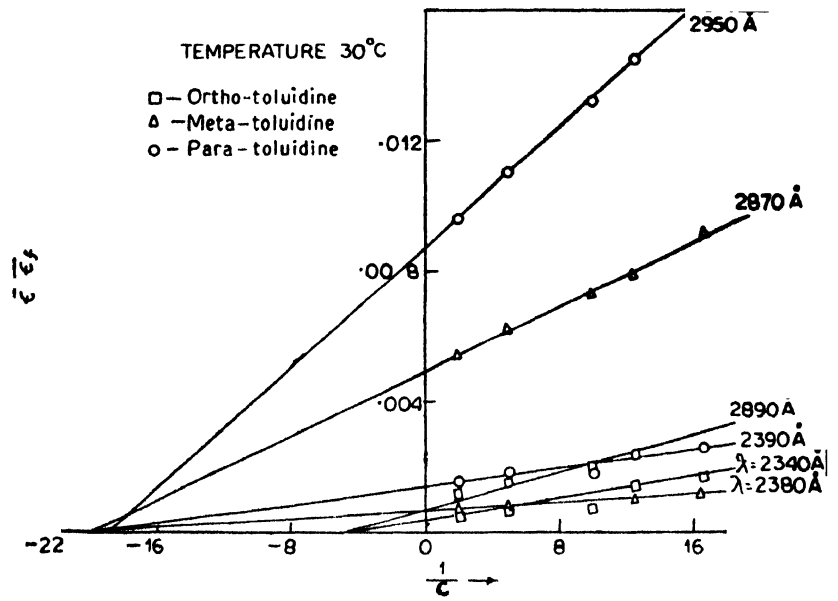

Fig. 1. Plots of $\frac{}{\varepsilon - \varepsilon_t}$ vs $1/C$ for the determination of K, the association equilibrium constant.

Now, molar extinction coefficients ε_b for the hydrogen bonded species were calculated for every wavelength from the equation derived from the eq, (1),

$$\varepsilon_b = \varepsilon + \frac{\varepsilon - \varepsilon_t}{KC} \tag{3}$$

By plotting ε_b against ν (frequency in cm^{-1}), the hydrogen bonded curve was obtained (Baba and Suzuki 1961; Suzuki and Baba 1963).

The energy of hydrogen bond formation (ΔH) is related to K and T (temperature in °K) by,

$$\Delta H = -\frac{Rd \ln K}{d(1/T)} \tag{4}$$

A plot of $R \ln K$ against $1/T$ yielded a straight line whose slope gave ΔH (fig. 2). In calculating ΔH and the association equilibrium constant K, method of least squares was used.

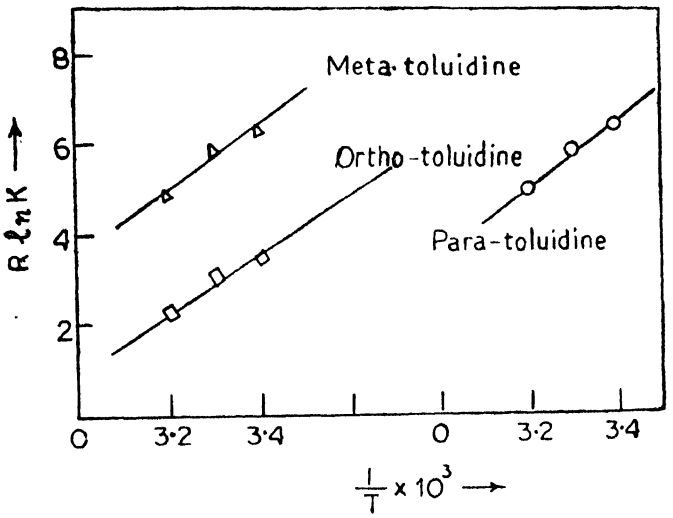

Fig. 2. Plots of $R \ln K$ vs $1/T$ for the determination of ΔH, the hydrogen bonding energy

The oscillator strengths (f) for the transitions of both the free (f_f) and the bonded (f_b) molecules were calculated from the well-known relation,

$$f = 4.32 \times 10^{-9} \int \varepsilon \, d\nu \qquad \ldots\ldots\ldots (5)$$

3. Results and Discussions

In cyclohexane solution the isomeric molecules of toluidines are found to yield two systems of absorption bands in the regions 2620 Å to 3090 Å and 2200 Å to 2550 Å. Both are due to π– electronic transitions and are designated as Transition I and Transition II respectively. The wave numbers of bands of the two systems, the oscillator strengths (f) and the frequency shifts due to hydrogen bond formation are given in the Tables 2 and 3. It is seen that with addition of proton-acceptor dioxane to the toluidine-cyclohexane mixture, there is a shift in the positions of the absorption maxima and the integrated absorption values $\int \varepsilon \, d\nu$ increase. These observations are similar to those reported by Baba and Suzuki (1961) in the case of phenols and naphthols and indicate formation of intermolecular hydrogen bond between toluidine and dioxane molecules.

In order to find out the effect of gradual increase in the concentration of the proton acceptor molecules on the formation of such bond, the value of the integrated absorption $\int \varepsilon \, d\nu$ has been plotted against dioxane concentration (fig. 3(a) and 3(b)) from which it can be clearly seen that in all cases and for both the electronic transitions, the value of the integrated absorption first increases and then tends to a constant value above a certain concentration ($\sim$0.5 mole/litre) thereby indicating that bond formation is almost complete at such concentration with formation of 1:1 complex between toluidine and dioxane molecules.

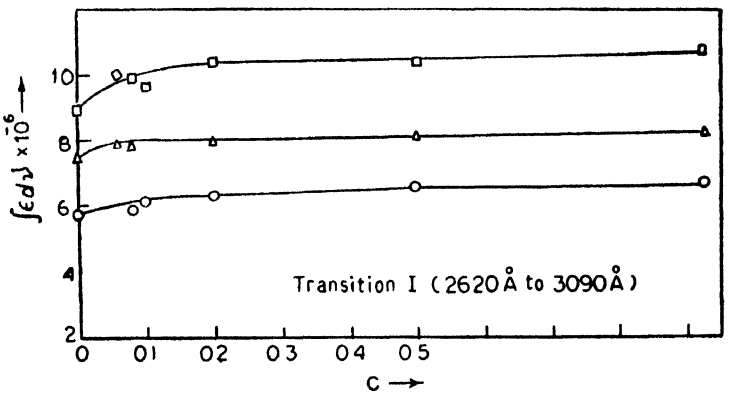

Fig. 3.(*a*) Plots of the integrated absorption $\int \varepsilon \, d\nu$ vs dioxane concentration C at the temperature of 303°K for the transition I.

□ -- ortho — toluidine
Δ · · meta — toluidine
O — para — toluidine

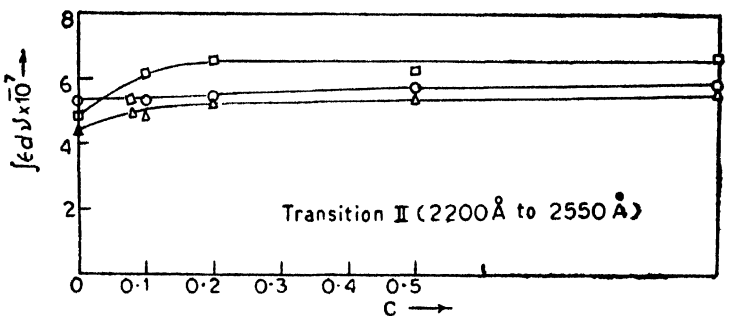

Fig. 3.(*b*) Plots of the integrated absorption $\int \varepsilon \, d\nu$ vs dioxane concentration C at the temperature of 303°K for the transition II.

For each electronic transition of the individual toluidines, the association equilibrium constant K (in litre/mole) was calculated for various frequencies at the three different temperatures 293°K, 303°K and 313°K.

For a particular toluidine system, K-values determined from the two electronic transitions agreed fairly well with each other as shown in the Table 1. From the linear graph obtained from a plot of $1/(\varepsilon-\varepsilon_f)$ vs $1/C$, it may be inferred that only one molecule of toluidine is associated with one dioxane molecule in the hydrogen bond formation.

Table 1. Data on equilibrium constants and thermodynamic parameters for the hydrogen bonding of the systems of isomeric toluidines, dioxane and cyclohexane

Systems	Temperature in °K	Association equilibrium constant K in litre/mole			$-\Delta F$ in kcals/mole	ΔH in kcals/mole
		Transition I (2620Å to 3030Å)	Transition II (2200Å to 2530Å)	Mean K		
ortho-toluidine	293	5.89	5.80	5.85	1.034	4.92
	303	4.64	4.60	4.62	0.925	
	313	3.058	3.00	3.034	0.698	
meta-toluidine	293	24.00	24.00	24.00	1.853	5.72
	303	19.92	20.67	20.30	1.815	
	313	13.00	12.30	12.65	1.558	
para-toluidine	293	25.00	25.00	25.00	1.876	6.17
	303	18.75	19.40	19.075	1.767	
	313	12.07	11.80	11.935	1.551	

From the measured values of ΔH, the hydrogen bonding energy it is found that ΔH is in the order,

$$p\text{-toluidine} > m\text{-toluidine} > \text{o-toluidine}.$$

Possible interaction between two reacting groups like NO_2 and OH in ortho-positions has been discussed by Sidgwick and Callow (1924). In the case of o-toluidine, one of the groups is CH_3 which is known to be practically inactive

Table 2. Intensity change due to hydrogen bond formation

System	Transition	f^*_f	f_b**	f_b/f_f	$\Delta f/f_f$	$\Delta f = f_b - f_f$
ortho-toluidine	I (2620-3030 Å)	0.03944	0.04648	1.178	0.1785	0.00704
	II (2200-2530 Å)	0.21340	0.29074	1.360	0.3624	0.07734
meta-toluidine	I (2640-3040 Å)	0.03226	0.03574	1.108	0.1079	0.00348
	II (2250-2550 Å)	0.19310	0.24192	1.25	0.2528	0.04882
para-toluidine	I (2730-3090 Å)	0.02516	0.02915	1.158	0.1526	0.00399
	II (2200-2520 Å)	0.23317	0.25542	1.095	0.0954	0.02225

* —free, —bonded.

Table 3. Frequency shift on hydrogen bond formation (frequencies in cm^{-1})

System	Transition	Assignment	ν_f	ν_b	$\delta\nu = \nu_b - \nu_f$	Mean $\delta\nu$
ortho-			33,888	33,773	(−115)	(−118)
	I	$'A' \leftarrow 'A'$	34,712	34,591	(−121)	
toluidine			42,359	42,181	(−178)	
	II	$'A' \leftarrow 'A'$	44,039	43,846	(−193)	(−185.5)
	I	$'A' \leftarrow 'A'$	34,954	34,772	(−182)	
meta-			34,525	34,375	(−150)	(−166)
	II	$'A' \leftarrow 'A'$	48,181	42,003	(−179)	
toluidine			41,828	41,653	(−175)	(−177)
	I	$^1B_2 \leftarrow {}^1A_1$	34,425	34,225	(−200)	
para-			34,354	34,178	(−176)	(−188)
	II	$^1B_2 \leftarrow {}^1A_1$	41,828	41,653	(−165)	
toluidine			42,540	42,359	(−181)	(−172)
			41,309	41,139	(−170)	

Table 4. Change of intensity with proton-acceptor (dioxane) concentration
Temperature : 303°K

Proton-donor concentration	Proton-acceptor (dioxane) concentration in moles/litre	$\int \varepsilon d\nu$
ortho-toluidine of conc.	0	9.13 × 10^6
6.0×10^{-4}	0.05	10.13 × 10^6
moles/litre	0.08	9.92 × 10^6
(Transition—I)	0.1	9.69 × 10^6
	0.2	10.41 × 10^6
	0.5	10.35 × 10^6
	Bonded (Calculated)	10.76 × 10^6
ortho-toluidine of conc.	0	4.94 × 10^7
3.1×10^{-5}	0.08	5.44 × 10^7
moles/litre	0.1	6.16 × 10^7
(Transition—II)	0.2	6.59 × 10^7
	0.5	6.25 × 10^7
	Bonded (Calculated)	6.73 × 10^7
meta-toluidine of conc.	0	7.47 × 10^6
3.35×10^{-4}	0.06	7.93 × 10^6
moles/litre	0.08	7.83 × 10^6
(Transition—I)	0.2	8.03 × 10^6
	0.5	8.17 × 10^6
	Bonded (Calculated)	8.27 × 10^6
meta-toluidine of conc.	0	4.47 × 10^7
3.35×10^{-5}	0.08	5.02 × 10^7
moles/litre	0.1	4.89 × 10^7
(Transition—II)	0.2	5.31 × 10^7
	0.5	5.40 × 10^7
	Bonded (Calculated)	5.60 × 10^7
para-toluidine of conc.	0	5.825 × 10^6
3.13×10^{-4}	0.08	5.96 × 10^6
moles/litre	0.1	6.21 × 10^6
(Transition—I)	0.2	6.37 × 10^6
	0.5	6.63 × 10^6
	Bonded Calculated)	6.75 × 10^6
para-toluidine of conc.	0	5.40 × 10^7
3.13×10^{-5}	0.1	5.39 × 10^7
moles/litre	0.2	5.51 × 10^7
(Transition—II)	0.5	5.78 × 10^7
	Bonded (Calculated)	5.91 × 10^7

and the C-H compounds are not usually listed as H-bonding acids. (Pimentel and McClellan 1959). Therefore any intra-molecular hydrogen bond, worthy of consideration, between the two groups CH_3 and NH_2 may be ruled out. The smallest value of ΔH in the case of o-toluidine should, therefore, be attributed to steric effect (Zanker and Wittwer 1959) of the methyl group in this molecule on the amino group in hindering intermolecular hydrogen bond formation with dioxane molecules. This conclusion is in agreement with that arrived at from infrared studies (Medhi *et al* 1962). From this consideration, it would further be expected that the change in ΔH will be greater in going from the ortho-to the meta-isomer than from the meta- to the para-isomer. The relative values of ΔH are in accord with this expectation.

The shift in frequency on hydrogen bond formation $\delta\nu = \nu_b - \nu_f$ has been measured, ν_b referring to frequency of absorption maxima for hydrogen-bonded system and ν_f to that for free molecules. It has been noticed that the band maxima shift towards longer wavelengths. The frequency shifts differ in magnitude in the case of the two electronic transitions I and II but for a particular electronic transition all the vibrational components show more or less uniform shift (Table 3) Another significant observation is (Table 2) that for both electronic transitions the oscillator strength (f_b) for the bonded molecules is always greater than that (f_f) for the free molecules.

From these results it may be reasonably concluded that formation of intermolecular N-H . . . . . O bond introduces larger interaction between lone pair electrons on N-atom and the ring π-electrons resulting in an increase in the migration moment. Following Baba and Suzuki (1961), it may be argued that under the influence of the electron donor oxygen atom, the σ-electrons associated with the N-H bond will be pushed towards the nitrogen atom and the resulting increase in the electron density around the nitrogen atom will lead to a decrease in the binding energy of the sp^2 hybridized lone pair of nitrogen As a result, their interaction with the ring π-system will increase, accounting for the enhanced intensity of the spectra of the hydrogen bonded species. Investigations with several similar systems are in progress.

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